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EDITORIAL

Alcohol

DR. E. F. ARMSTRONG has delivered an excellent Jubilee Memorial Lecture entitled "Alcohol through the Ages," the publication of which we complete in this issue. Its title clearly indicates the scope of the lecture for it traces the use of alcohol from the earliest days when its use was restricted to its consumption as a drink down to the present time when it is the basis of an important chemical industry and the raw material from which many interesting and valuable compounds are prepared. Vast as is the literature that contains allusions to wine or beer and innumerable as are the books that deal with those cheerful beverages, the making of them is older, far older, than any writings that have come down to us; indeed the use of alcohol must have long preceded the invention of an alphabet or any other form of writing. The ingenious author who described in such detail the discovery of roast pig did not dare to give an account of the discovery of wine; it was in such far-off prehistoric days that even Lamb's imagination could hardly have conjectured the conditions of human society. The discoveries of the last hundred years have traced our civilization back to a much earlier period than our ancestors believed to be possible and the earliest written records we possess—and possibly we shall not discover any earlier ones—show us a society that had attained a very high degree of civilization, languages with a degree of complexity that would now be intolerable to us, great skill in the working of metals, in architecture, and in agriculture. In a few subjects we have far surpassed them in modern days, and chemistry is one. Since the time of Priestley, Lavoisier, Berzelius, and the other great men who laid the foundations of our science, chemists have with ever increasing speed been busy in completing the edifice and are perhaps already now furnishing it with innumerable refinements and adorning its garden, greenhouses, and garages. In any case chemistry is probably the greatest advance that mankind has made since the days of Tubal-Cain and some others whose biographical details are unduly scanty. Dr. Armstrong has easily and pleasantly surveyed this great lapse of time so far as concerns alcohol and whether we read his lecture with an eye on the past, or both eyes on the future, we should be equally grateful to him. Our gratitude might also be extended to Dr. Messel, whose generosity has enabled the Society to organize the noble series of lectures of which this is the latest.

Atomic Nuclei and the Neutron

As long ago as 1920—and thirteen years is a long time in the life-history of modern atomic physics—the possible existence of the neutron, by which we mean a proton and an electron closely associated to produce a particle of approximately unit mass and of zero charge, was already under discussion. In that year Lord Rutherford discussed its probable properties in the Bakerian Lecture, and experiments, which were in fact unsuccessful, were instituted in the Cavendish Laboratory to detect their formation. Much as we feel we know about the behaviour of electrons, the spectroscopic manifestation of their movements, and the effect of their presence or absence on the chemical properties of an element, we know extremely little about the nuclei of atoms. We know of course, that some must contain protons and that some afford alpha-particles on disintegration; also we are compelled to assume that electrons share in their structure, or atoms would not be electrically neutral. Gradually, however, experimental observations are being made which will one day be welded into a comprehensive and scientific theory of nuclear structure. Already it has been established that bombardment with α-rays releases protons, and that bombardment with highly accelerated protons in at least one case releases α-particles. We have become familiar with the idea of isotopy and its bearing on both chemical relationships and atomic weight determinations, and we are now intrigued by the annouucement of the discovery of a hydrogen isotope of mass 2. We have indications of the existence of nuclear energy levels, and nuclear gamma-rays are now believed to be due to the transition of an α-particle between energy levels in an excited nucleus. But this line of attack on the nucleus will, as Lord Rutherford said last year in a discussion on the structure of atomic nuclei, entail many years of work on the gamma-ray spectrum, which will need examination

with the greatest possible precision. In other work the protons liberated from aluminium by the α-particles of polonium have been resolved into eight distinct groups connected in pairs. Our knowledge of atomic structure has been enriched during the past year by important contributions which have provided us with strong *experimental support for our belief in the existence of neutrons*, and have therefore enabled us to abandon our assumption of the presence of free electrons in nuclei. Such a structural unit may be regarded as composed in the way we have indicated, or it may be an independent fundamental entity. In any event it appears to have unit mass and zero charge, it passes through matter unchanged except on direct collision with the nucleus of an atom, and in the latter event it is the cause of atomic disintegration. Neutrons are produced by bombarding beryllium or boron with α-particles from polonium. It was first observed that a very penetrating radiation is thus produced, and then that this radiation ejects high-speed protons from matter containing hydrogen, such as paraffin wax. Further investigation showed that other elements, for example, lithium, helium, and beryllium were similarly affected. The quantum hypothesis of the radiation would involve denial of the conservation of energy and momentum, and *hence the existence of the neutron, which is the* alternative explanation of the experimental facts, is affirmed. When liberated, the neutron has a velocity about one-tenth of that of light. Whether it is regarded as a small dipole or as a proton embedded in an electron, its "radius" is between 10^{-13} and 10^{-12} cm., and its mass probably between 1·005 and 1·008. Experiments on the effect of neutron radiation on nitrogen have afforded evidence of the disintegration of the nitrogen nucleus by this means; the first evidence for artificial disintegration by α-particles was afforded also by nitrogen. In the former case the disintegration is supposed to proceed thus: $n^1 + N^{14} \rightarrow He^4 + B^{11}$, and in the case of oxygen to be represented by: $n^1 + O^{16} \rightarrow C^{13} + He^4$. *With nitrogen, other possibilities indicated by* some of the results are the liberation of a proton ($N^{14} + n^1 \rightarrow C^{13} + H^1 + n^1$) and of the isotope of hydrogen ($N^{14} + n^1 \rightarrow C^{12} + H^2 + n^1$). Naturally there is now a competition, and a very laudable one, to use these new results in constructing a model of the simpler atomic nuclei. We confess to a liking for models, for they help one so enormously to understand the realities of complex situations, and it is always rather disappointing to learn that, after all, they are unreal and quite meaningless.

Round the Gas Industry

The carbonization of coal for the purpose of making gas is the *largest chemical industry, employing more* capital and more workpeople than any other section. Consequently, the annual statements of the leaders of the industry are awaited with special interest as likely to indicate the trend of new developments. The gas industry never stands still: in the past, hampered by legislation and prevented from expanding into large units, it has devoted its energies to the perfection of the technical side of gas making, with the result that we have led the world in this respect. To-day two other subjects are in the forefront of interest, viz., a more active sales policy forced on the industry by the competition of fuel oil and electricity, and the important question of the amalgamation of the smaller companies into larger units with the ultimate thought of a gas grid which would make use also of the gas produced by coke ovens and eventually, perhaps, by low-temperature carbonization plants and oil refiners. Gas and gas coke are in severe competition with electricity, which is still specially favoured by the State, and with imported fuel oil which, strange to say, comes in untaxed. Consequently, the price at which gas can be sold to the consumer is of importance. The coal industry has no better customer than the gas industry, and it would be greatly to its advantage to encourage the more widespread use of gas, yet, as Dr. Carpenter so trenchantly emphasized, a gas works actually has to pay more for its coal than a purchaser of the same coal for other purposes would do. The difference in price on the two million tons of coal which is gasified in South London means an excess expenditure of at least £150,000 on the coal bill as a result of the operation of the Coal Mines Act. A feature of the year's working of the industry is the ever-increasing production of benzole, our only native motor spirit. The advantage of this is reflected in the accounts of the Gas Light & Coke Company, which has throughout the year removed the benzole from the gas produced at its Beckton station by means of active carbon. It is expected that the 28 million gallons of refined benzole produced by the gas and coke-oven industries during 1931 will be materially increased in the near future, as other gas undertakings are known to be installing active carbon or oil washing plants to recover benzole: less than one-third of the possible total quantity is at present recovered. A second feature on the products side of the gas industry is the increasing success which is attending the use of creosote fuel for engines: for example, a mixture of creosote and naphtha is being sold by the Belfast Corporation at fourpence per gallon. Although such a fuel is available in too small amount to have a universal distribution, it will be very economical for omnibus and lorry services which can draw it from a central source of supply. On the gas side, the chairmen of both the big London companies call attention to the progress that gas lighting under pressure is making in all the principal thoroughfares in the metropolis, a subject we have previously commented on. Experimentally, but with increasing hope of success, trials are being made with compressed gas in cylinders for use in motor vehicles. The Gas Undertakings Act of 1932 has given the industry generally power to invest money in other gas undertakings, or in allied industries, such as were already possessed by certain companies. Some of the first fruits of this are seen in the action taken by the Gas Light & Coke Company to obtain a controlling interest in a company which owns certain gas undertakings on the South Coast. There are private Bills in Parliament which seek to obtain for the industry the right to compete for business with the same freedom as is enjoyed by oil and electricity. Further, Government legislation to help the industry is long overdue: its prosperity will help the coal mines and reduce unemployment.

MODERN SUSPENDED ARCHES

Latest Scientific Principles of Furnace Construction

It is well known that for water-tube boiler settings and many types of large combustion chambers in the metallurgical industries the ordinary simple sprung firebrick arch is now obsolete, and has been replaced by the suspended arch. Essentially this is a series of standard firebrick blocks, each attached independently to overhead steel girders or beams, forming a flat arch or roof, and the matter is of considerable interest in connexion with various types of combustion chamber used in the chemical and allied industries.

The latest scientific principles of design in this field are represented by the "Liptak" double suspension arch, manufactured, with the "Bigelow" single suspension arch and suspended combustion chamber wall, by Liptak Furnace Arches, Ltd., of London. Many installations are at work in glass, ceramic, annealing, axle-hardening, drop stamping, reheating, and billet heating furnaces, while in connexion with the application to water-tube boilers numerous power stations are equipped with the "Liptak" arch, as well as the "Bigelow" wall. For example, there may be mentioned an installation of

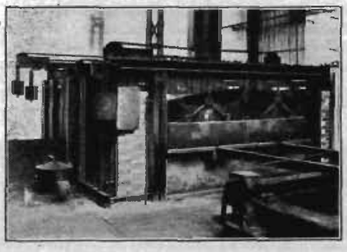


Fig. 1

Axle-hardening furnace fitted with a Bigelow flat roof

eight arches, 10 ft. long by 24 ft. wide, on "Babcock & Wilcox" boilers at a well-known power station in Great Britain, while "Bigelow" front arches are being equipped on eight new "Stirling" boilers now being installed at the Copenhagen Electricity Works (Denmark).

In general the arches are constructed of a series of strong and heavy steel beams of "H" section fixed across the roof of the combustion chamber, having attached underneath a series of cast-iron brackets carrying cast-iron hanger beams.

One of the most valuable features of the "Liptak" arch, different from any other method of arch construction, is the double suspension; that is, smaller standard firebrick blocks of high-grade quality are suspended from the hangers, made of the correct shape, with recesses to engage with the latter forming a reserve arch. To these smaller firebrick blocks are now attached larger firebrick blocks of the same type, formed with a suitable recess or neck at the top to engage with a corresponding projection at the bottom of the smaller reserve blocks. In this manner a flat roof is formed of two separate layers of blocks one above the other, which enormously increases the margin of safety, since if by any chance one of the lower blocks burn out there is no harm done as the second upper block comes into operation. Also

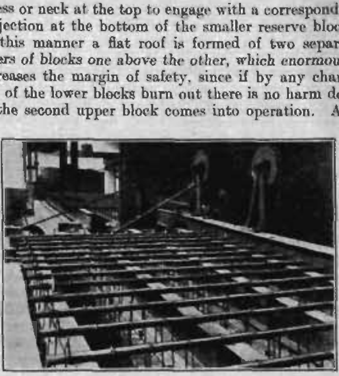


Fig. 2

Reheating furnaces fitted with Bigelow flat roofs

each of the larger or main blocks is made with waved or corrugated sides so that pieces do not easily fall out if a block becomes broken.

A main advantage of the suspended arch is that almost any width can be constructed, depending merely on the strength of the steel beams; for example, "Liptak" arches 30 ft. wide and over are operating. Also the ordinary sprung arch is the wrong shape for efficient and uniform heat radiation, while further, in the suspended arch each block is entirely independent of its neighbours, being attached to the steel beams above, and therefore not subjected to any lateral strain, being also easily and quickly replaced.

ALCOHOL THROUGH THE AGES

JUBILEE MEMORIAL LECTURE

By E. F. ARMSTRONG, D.Sc., Ph.D., LL.D., F.R.S.

(Concluded)

The Preparation of Absolute Alcohol

Under normal pressure alcohol and water form a constant boiling mixture of approximately 96% alcohol content, and until recently it was impossible to obtain commercially a stronger spirit in large quantities. Making use of the experimental work of Sidney Young (J.C.S., 1902, 81, 710), namely, by adding a third liquid which reduces the partial pressure of the alcohol to a far greater extent than it does that of the water, it is possible to destroy the constant boiling mixture and produce, by fractional distillation, an alcohol which is absolute. By far the largest proportion is made by these azeotropic processes, which are based on the formation of a ternary alcohol–water–third liquid mixture of appreciably lower boiling point than either pure alcohol itself or any of the other possible binary mixtures of the three components. Various "third liquids" or so-called entrainers have been proposed, the one most

largely used being a mixture of benzene with a special petrol fraction of limited boiling-point range.

Such azeotropic processes are easily made continuous. From the steam-heated dehydrating column charged initially with a certain quantity of the entrainer and fed continuously with the aqueous alcohol to be dehydrated the absolute alcohol is drawn off at the base. The ternary vapour mixture issuing from the top of this column separates on cooling into two liquid layers. The upper layer consists mostly of entrainer, together with smaller proportions of alcohol and water, and is returned at once to the dehydrating column. The lower layer contains most of the water of the ternary mixture, accompanied by small amounts of entrainer and alcohol. This layer may be freed, in a small purifying column, from entrainer (as ternary mixture), leaving only aqueous alcohol, which is easily rectified to about 95% (by volume) strength, prior to return to the dehydrating column. Unavoidable small loss of the volatile entrainer occurs, but means are now adopted which reduce such loss to almost vanishing point. These azeotropic processes may be carried out either at ordinary or at increased pressure, and it is a matter of controversy whether the advantage of obtaining a ternary mixture of higher water-content by working at several atmospheres pressure is not more than counterbalanced by other obvious disadvantages.

By suitable arrangement of plant the separation of the alcohol from the original dilute alcoholic liquid (such as fermented molasses solution), the concentration to about 95% strength, and the final dehydration are combined to make what may be regarded as a single operation, during which also the volatile impurities and high boiling point impurities of the original liquid may be removed.

Previously, the use of solid dehydrating agents, of which lime and calcium carbide were commercially the most important, was necessary when anhydrous alcohol was desired. The researches of Young pointed the way, though it was some years before the azeotropic process was developed on a large scale. The pioneers have been the French at Melle and the U.S. Industrial Co. at Baltimore, both of whom have extensive patent rights. In the Melle process ordinary pressure is used: the Americans work under increased pressure. Whilst the process revolutionized the production of alcohol stronger than 96% and made it possible to produce absolute alcohol as a raw material for chemical operations, its importance has been much increased by the potential use of alcohol as a motor fuel, for which purpose it is required in the dry state. The method practised by the Distilleries des Deux-Sèvres has been described elsewhere (Chim. et Ind., 1931, **25**, 26; cf. Wagner, Z. Spiritusind., 1930, **53**, 260). A very full summary of the azeotropic process, with diagrams, has been given by Dietrich (Z. Angew. Chem., 1932, **45**, 233), so that it is unnecessary to go into it here at any great length. The essential points of any process are the design of the apparatus and the nature of the added liquid.

Among suitable third liquids, called ternary agents, are benzene, toluene, hexane, carbon tetrachloride, ethyl acetate, ethylene dichloride, etc.; they have the property of being quite insoluble in water containing only a little alcohol. The economic advantage of handling liquids only in place of solids, and the sparing of steam in fractionation, make this azeotropic method the superior one for the production of alcohol on the large scale. *The product is 99·9% absolute, and it has the following physical constants*: $d_{25} = 0·78523$. B.P. = 78·38°.

A smaller, but still appreciable, amount of absolute alcohol is made by direct dehydration of aqueous alcohol by means of solid water-combining materials. Quicklime is used to a limited extent for this purpose and here too the action may be carried out either at atmospheric or at increased pressure. A dehydrating agent which has come into more common use in recent years consists of a mixture of sodium and potassium acetates (Gorhan process of H.I.A.G.). An absolute alcoholic solution of the mixed acetates flows down a ring-packed column and meets the ascending aqueous alcohol vapour, abstracting its water and reaching the base of the column as an aqueous solution of the acetates. The absolute alcohol vapour passes from the top of the column to a condenser, and the condensate is partly run off as finished product and partly used to dissolve fresh acetate mixture. The aqueous acetate solution from the bottom of the column is passed over coils carrying superheated steam and is thus dehydrated prior to re-dissolution in absolute alcohol. By utilizing the heat of the used superheated steam, this process is made to work with a low steam consumption, but against this the alcohol treatable by the process must apparently be of more than usual purity—for industrial alcohol—in order that the dehydrating capacity of the salts may be retained unimpaired.

To-day the German State Alcohol Monopoly is said to be using trichlorethylene instead of benzene in six of its plants obtaining a daily yield of 70,000 gallons of absolute alcohol, which is used for power purposes. The last traces of ternary agent may be removed by passage through active carbon, whereby a tasteless, odourless, pure alcohol is obtained.

The methods of dehydrating alcohol in the laboratory are too well known to need description. The removal of the very last trace of water is not an easy matter, and probably few chemists have ever had 100% alcohol in their hands. Among them will be the pupils of Ludwig Claisen, whose work in acylation over thirty-five years ago did much to lay the foundation of some of our modern theories of structure.

Alcohol as a Source of Power

Although power alcohol no longer has the advantage of novelty, it is a factor of increasing importance, in view of the rapid development of mechanical transport. The commercial value of this new motor fuel has been tried and proved, and practically every country has provided by legislation for its manufacture and use. In Germany and France especially the use of this "Alcohol motor fuel" was instituted several years ago. It is only in the British Empire that we find the manufacture of power alcohol for commercial purposes comparatively neglected. The exceptions to this statement so far are Southern Rhodesia, Natal, and Queensland.

The economic practicability of power alcohol depends largely on the fact that absolute alcohol can be produced by the azeotropic process at a cost equal to that of distilling 96% spirit. The difficulties of the limited miscibility of 96% spirit are overcome and about 15% of absolute alcohol can be safely added to petrol without any adjustment to carburettor or engine being required. The mixture forms an improved fuel which is no more hygroscopic than petrol and has no increased oil solvent properties.

In those European countries which have no petroleum supply, the study of substitutes for imported petrol is a major problem of both national economics and defence. Where alcohol can be made in quantity from maize, potatoes, beet, or cheap carbohydrate material its use will help the farming industry; where it can be derived from a waste product, as in Sweden from the sulphite liquor of the wood pulp industry, it is of obvious value to find a use for it. Hence, most countries have been active in studying the use of alcohol motor fuel and great progress has been made, particularly in France. There is a summary of the present position in *Chimie et Industrie* (1932, July) and in the *International Sugar Journal* (1932, p. 26).

In consequence of their ability to produce alcohol from vegetable sources cheaply, most countries have enacted by legislation that all petrol sold must contain a minimum proportion of alcohol, and they have national programmes in hand to manufacture and rectify considerable quantities of it. Germany and Poland make 6% of alcohol compulsory, but a new plan for the entire reorganization of the supply of motor spirit in Germany was announced early in 1932.

The new policy aims at using domestic sources of supply to a much greater extent than hitherto, and at restricting imports of foreign petroleum. It therefore provides for exclusive marketing of a standard mixture at a uniform price and for importation by quota or licence. The formula for the standard mixture, propounded with a reserve at this early stage, is: vegetable alcohol 10—12%, industrial alcohol 8—10%, benzol 10%, petrol 70%. The vegetable alcohol would be furnished by German agriculture through the spirit monopoly, and the industrial alcohol and benzol by German industry. It is estimated that the relatively high cost of the vegetable alcohol would be counterbalanced to some extent by the relatively low cost of the industrial product. About half of the petrol, of which the estimated total requirement is 1500 tons, would be supplied by the Leunawerk of the I.G., using its synthetic process and the new cracking plant of the Prenssag at Miesburg. About two-thirds of the 75 million gallons of alcohol produced is derived from potatoes.

A suggested Italian national fuel is 40% petrol, 35% ethanol, 25% benzol. An intensive study of the development of an alcohol industry is being made by the State. France at one time made 25—35% of alcohol compulsory, but has withdrawn the law, which could not be enforced owing to the lack of sufficient alcohol at the price offered. The raw materials are costly in France, where there are a number of small distilleries. It was the first country to make the purchase of alcohol compulsory by the oil companies. Much of the alcohol mixture produced is used in the Paris omnibus service.

Natal and Queensland in our overseas Empire use an alcohol fuel. In England, in the absence of supplies of ethanol seeking an outlet, its use has not been made compulsory, though the necessary experimental work for its manufacture and use had been done.

The use of pure alcohol in the present engine is impracticable, but mixtures of petrol with 15 to 25% ethanol make a better motor spirit than petrol alone. The addition of some proportion of ether has also been studied: it gives increased volatility, as well as a lessened tendency for the constituents to separate even at very low temperatures. Alcohol further has an important cleaning effect in lessening the deposit of carbon. One of the criticisms of alcohol has been that when any quantity of water is present the mixture tends to separate into two layers; thus in a mixture of 70 petrol + 30 alcohol the addition of 1·3% water causes separation.

The presence of alcohol improves the volatility of the fuel as it forms an azeotropic mixture: further, owing to its high latent heat the vapours entering the cylinder are colder, so that a greater charge is taken in at each stroke.

The economics of the use of alcohol depend entirely on the relative prices of petrol, including any taxation, and alcohol, and the amount of restriction or encouragement put by the Government in the way of its use.

In Australia, where the Shell Co. is marketing Shellpol containing 15% ethanol in agreement with the distilling interests, and in South Africa, vegetable matter, and therefore alcohol, are cheap, whilst petrol has to be transported a long way. Elsewhere, as already indicated, governments are forcing its use to save money from being spent abroad.

In this country the position may at any time change suddenly: at present we are content to spend very large sums annually on foreign oil, which exchange difficulties may make it desirable to replace by alcohol. In the latest regulations the denaturants specified for power methylated spirits are 2½% wood naphtha, ½% crude pyridine and 5% of petrol or benzol, together with a dye spirit, red III.

Generally speaking, ethanol should not be regarded as replacing petrol, but on account of its anti-knock value, higher compressibility, quicker pick-up, and other qualifications as tending to enhance the value and extend the use of petrol. There is a possibility further that some day the similar application of methanol may be successfully achieved: this would give a means of making one constituent of motor-spirit from coal and supplement the benzol obtained from coal in quite another manner: the trouble of separation into two layers is far worse with methanol than with ethanol.

Alcohol–benzol motor fuels have been studied in this country as representing an all-British mixture. The data relating to them are collected in "Motor Benzole" (Hoffert and Claxton). The London General Omnibus Company made extensive trials (Engineering, 1920, **110**, 623), the best results being obtained with a mixture of 70 parts of benzol to 30 parts of alcohol.

From the economic point of view particularly the advantages to be derived from the use of alcohol lie in a market for surplus agricultural products on the one hand, and the cheaper cost to the fuel consumer on the other. For instance, it has been estimated that three distilleries in South Africa could produce annually 12 million gallons of alcohol, making, with petrol, 86 million gallons of the new motor fuel to be sold at 1s. 6d. per gallon at the coast and 1s. 9d. inland. Having regard to the cost of imported petrol and its retail price in that Dominion, the great saving to the consumer there is at once obvious. Again, with maize on the "free list," the conversion of a great part of the surplus crop would prove a tremendous boon to the producer, with feed for his cattle as a valuable residue; and he could sell meat to England instead of maize.

Alcohol as a Source of Light and Heat

About the middle of last century alcohol had a considerable vogue as an illuminant, its non-luminous flame being rendered luminous by the addition of turpentine, which by itself burns with a very smoky flame. It has also been used particularly on the Continent in lamps provided with an incandescent mantle as it is odourless and smokeless, gives a more uniform light, and is safer than kerosene.

Its use in spirit lamps requires no comment. Less well known is the solid spirit made by mixing denatured alcohol with 5 to 7% of soap, which is produced within the spirit from stearin and sodium carbonate. This material packed in suitable small tins has found a very large use as a portable spirit lamp for camping etc. on the Continent and in America, though it has found little favour here. A similar product containing nitrocellulose and alcohol has a large use.

The Industrial Uses of Alcohol

These are too numerous and well known to require mention in any detail. Primarily alcohol is used as a solvent in the industrial arts, when sometimes it remains part of the finished article, as in varnishes, lotions, sheep dips, dye solutions, and collodion. At other times the alcohol is recovered after the operation.

Some of the fine chemicals made from alcohol are of some antiquity as far as chemical products go. We may instance: ether, ethyl chloride, iodide, and bromide, chloral, chloroform, bromoform, and iodoform. In the aggregate these fine chemicals constitute an important outlet for industrial alcohol, but as their name implies, no one of them is manufactured on a really large scale comparable with those we shall mention in the next section.

We may refer here to the use of alcohol in the form of 96% grain spirit in perfumery. It is bought on odour, each separate package being tested. As it pays duty unless exported, it will be clear how great a handicap is being carried by the perfumery trade. The high Excise Duty on ethyl alcohol has reacted adversely on the perfume trade in England, making these products cost more than the public is prepared to pay for them. As a result, cheap and inferior perfumes are being made with alcoholic substitutes, in particular isopropyl alcohol, on which no Excise Duty is payable. Recently a denaturing formula has made the use of industrial alcohol in perfumes possible.

Ether from Alcohol

Ether is nearly as venerable a substance as alcohol. It was known as early as the 13th century, and its preparation from alcohol and sulphuric acid was described by Basil Valentine and Valerius Cordus (1540). Frobinius first named it *spiritus ætherens* or *vini vitriolatus* in 1730: it was then considered to be a sulphur compound, and it was not until 1800 that Valentine Rose proved this idea to be erroneous. Such famous chemists as Dumas, Liebig (1837), and Regnault worked on its constitution, but, as is well known, it was Williamson (1850) who established the views we now hold as to its constitution and the method of its formation in two stages. In particular he showed that amylethylether was obtained from amylsulphuric acid and ethyl alcohol. The now standard continuous method of preparation is due to Boullay.

Williamson's famous essay on etherification was first published in a paper read before the British Association at Edinburgh. At that time it must be remembered the constitution of organic compounds was unknown. What he did was to show that ether was not derived from alcohol by the abstraction of water, but the molecule of each contained the same amount of oxygen.

In an 18th century book, under the heading of the true art of preparing ether, it is stated that the preparation of this singular fluid has long been confined to a very few hands, the several published processes having mostly been of very precarious success and some of them even accompanied by serious danger to an incautious or unskilled operator. A detailed receipt is given, emphasis being laid on the haste and violence with which the alcohol is made to boil. Its modern uses as a solvent and in medicine, particularly as an anodyne, were evidently well known one hundred and fifty years ago.

Prior to the war period ether was always made by a batch process. Alcohol (4 parts) and sulphuric acid (3 parts) were heated in a lead-lined still at 140° and the alcohol and ether distilled off and separated by fractionation. By the addition of aluminium sulphate the reaction temperature could be lowered to 120°.

When very large quantities of ether were required as a solvent for propellant explosives during the war, ether replacing acetone, a continuous process was developed at Gretna, devised by Barbet, which became a model for subsequent operations of this type. The plant consisted of an alcohol vaporizer, a reaction still built of lead-lined steel, and a copper fractionating and rectifying column. The still is started with a mixture of 78% sulphuric acid and 92% alcohol at 105°. Alcohol vapour is then admitted and the temperature raised to 128°, at which it can be maintained by the heat evolved in the reaction. The vapours from the still are scrubbed with a 2% caustic soda solution to remove acid, and are then rectified, pure ether being withdrawn from one point of the column and anhydrous alcohol from another. Such a plant not only had a large throughput, but it gave an over-all yield of 94%

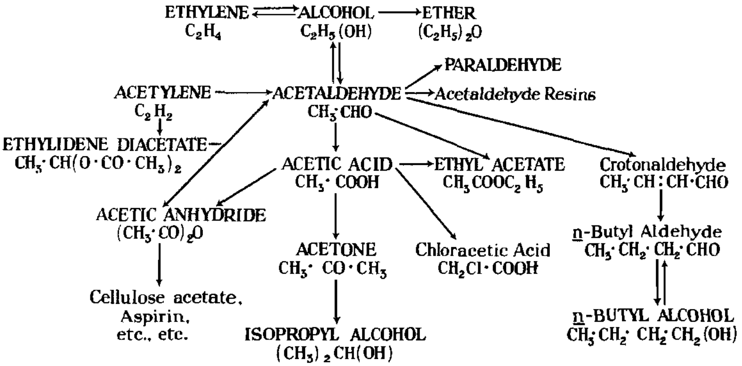
measured on a continuous total production of 500 tons of ether.

The Industrial Synthesis of Aliphatic Organic Compounds from Ethyl alcohol

Ethanol is very easily converted into aldehyde; aldehyde is the starting point for a long series of syntheses; it can also be made directly from acetylene. Ethanol, as we have seen, is manufactured by fermentation or from ethylene. Thus means are available by the use of catalytic processes for the industrial synthesis of a number of useful products on a large scale from the simplest unsaturated hydrocarbons.

The scheme of operations is set out in the following diagram:

The mixture of these, together with unchanged alcohol and water, passed into a large continuous still of the Barbet type, where they were separated, the alcohol being returned for a second passage and the aldehyde being rectified till it was of 98% to 99% average purity. The hydrogen was of 93% purity and contained about 4% of methane. The operation of such a still requires expert management and the process demands a good deal of refrigeration. In these and the following processes it is amazing to see carried out on the large scale, with high yields of pure substances, operations which even in the laboratory in glass vessels require numerous precautions. The technique of such catalytic operations shows how high a standard chemical engineering has attained.



Aldehyde from Ethanol

Two processes have been used in this country:

(1) Oxidation of ethanol in presence of a silver catalyst $C_2H_5 \cdot OH + O = CH_3 \cdot CHO + H_2O$.

(2) Dehydrogenation of ethanol in presence of activated copper $CH_3 \cdot CH_2OH = CH_3CHO + H_2$.

The former is worked by British Industrial Solvents, Ltd., at Hull; the latter was successfully used during the war by Joseph Crosfield & Sons, Ltd., at Warrington.

In the Hull process alcohol vapour is mixed with a definite amount of air and passed over a silver gauze catalyst. It is necessary to have a very rigid control of temperature, rate of flow, composition of vapours and other factors. The reaction is exothermic, so that once it is started no external heating is required. The yield is very good, and the vapours only require fractionating to pure aldehyde and unchanged alcohol. The greater part of this plant is constructed in aluminium; on account of the low boiling point of aldehyde an elaborate condensing system is requisite.

In the Crosfield process, alcohol was circulated over a highly active copper catalyst, prepared in a special manner, in tubes which were kept at about 280° C. During each passage over the catalyst about 20% to 25% of the alcohol was converted into aldehyde and hydrogen.

Acetone from Ethanol

Ethanol when passed over an iron lime catalyst under suitable conditions is largely transformed into acetone $CH_3 \cdot CO \cdot CH_3$. *Acetone is also produced on a* large commercial scale by Commercial Solvents, Ltd., in Indiana, U.S.A., together with butanol, by fermentation with a special organism.

Acetic Acid from Ethanol

Ethanol is first oxidized to aldehyde, which is further oxidized to acetic acid. There are two practical processes, namely, that worked at Shawinigan, in which a batch of aldehyde is oxidized by air in presence of manganese acetate, and the continuous process worked at Hull, in which aldehyde dissolved in acetic acid is continuously oxidized by air in a closed circuit, from which a fraction of the acid at about 95% strength is continuously removed. In either process a rectification gives glacial acetic acid of the highest quality. In both of them a rigid scientific control at every stage is necessary. Apart from the reaction towers, the plant largely consists of scrubbing towers and condensers. The question of corrosion presents great difficulties and offers opportunities for the skill of the chemical engineer.

The plant at Hull is capable of making 10,000 tons of acetic acid per annum: incidentally, from it glacial acetic acid was obtained on a large scale for the first time in this country. There is a large plant using the batch process at Billingham. The practical operation of this process is attended with two dangers, the formation of explosive mixtures of aldehyde with air or oxygen and the formation of peracetic acid during the operation. The oxidation apparently goes by way of peracetic acid as an intermediate product, and at low temperatures there is a risk of this not being decomposed as fast as it is formed and therefore accumulating in the reaction mixture.

There is an abundant literature relating to peracetic acid, though the text books so far contain little about it. Its relation and that of acetyl peroxide to acetaldehyde is brought out by the following formulæ:

$CH_3 \cdot CHO$	$CH_3 \cdot COOH$	CH_3CO_3H	$CH_3CO \cdot O \cdot O \cdot CO \cdot CH_3$
or AcH	Ac·OH	AcO·OH	AcO·OAc
Acetaldehyde	Acetic acid	Peracetic acid	Acetyl peroxide

Peracetic acid is a liquid above 0·1° C.; it explodes violently when warmed to 110°. Acetyl peroxide is a solid: it has m.p. 30°, and like peracetic acid is highly explosive, decomposing to methane and ethane. It has an odour resembling that of ozone. Either substance can be made by cautiously treating acetic acid or its anhydride with oxidizing agents, such as the peroxides or Caro's acid.

n-Butanol from Ethanol

This process is carried out in stages. Aldehyde obtained from ethanol is condensed to aldol in presence of alkali under rigidly controlled conditions, such as the proportion of water etc. On steam distillation the aldol breaks down into crotonaldehyde, which must be hydrogenated to give the same normal butanol as is produced by fermentation. The process is carried out either in one stage or in two separate stages, the first product being butyraldehyde. Butyl alcohol according to a recent patent can also be made in one operation from ethanol, when it is passed, together with hydrogen, over a special catalyst.

Ethyl Acetate from Alcohol

Large quantities of this product are at times required by the solvent industry so that an impetus was given to convert the old batch esterification process of acetic acid into a continuous one, which is considerably more economical. Very pure ethyl acetate is the final product of the stilling system; weak sulphuric acid is eliminated. A rival process uses acetaldehyde direct without the necessity of first making acetic acid. The aldehyde is polymerized by means of aluminium ethylate:

$$2CH_3 \cdot CHO = CH_3 \cdot COOC_2H_5$$

When a little anhydrous aluminium chloride is also present the yield exceeds 90%. It has been claimed that this process is so economical that it may pay to hydrolyze the ethyl acetate and so manufacture glacial acetic acid.

It has been sought (B.P. 1930, 312,345) to produce ethyl acetate from alcohol in one operation by means of a dehydrogenating catalyst, such as one containing 1 part of magnesium oxide, 4 parts of zinc oxide, and 20 parts of cupric oxide. Under suitable conditions the condensed liquor passing over the catalyst contains 20% by weight of ethylacetate. Even better results are claimed from mixed chromite catalysts containing zinc, copper, and cadmium. In such reactions, however, a complex mixture of products is obtained, and it would appear more rational as a rule to carry out the transformations from ethyl alcohol to other substances by stages, using at each stage that catalyst and those conditions which give the highest yield of the product desired.

Vinegar from Alcohol

A fairly recent use of industrial alcohol is in the manufacture of vinegar. Commercial vinegar is either produced by bacterial oxidation after fermentation of saccharine material or is diluted acetic acid. It is possible to prepare vinegar by bacterial oxidation of dilute alcohol, so obtaining a product which is purer and more regular in composition and of milder flavour than that prepared in the usual manner. The dilute alcohol nutrient mixture is sprayed over beech shavings packed in earthenware towers and impregnated with the bacillus. There is a wonderful plant in existence, consisting of 960 units, all of which are controlled electrically from a common centre, so that definite quantities are sprayed at definite intervals. It gives an eerie feeling to stand in this factory, where the human element is absent except as a watchman, whilst all around in silence and without fuss the enzymic agents are busily at work: nowhere else have I been brought so close to an understanding and admiration of the silent processes which are happening under similar directed control in plants and animals.

The Reactions of Alcohol

In the text books of a decade past, when the use of catalysts was in its infancy, the transformations to which alcohol lent itself were restricted in number. To-day, by varying the catalysts, the temperature, and the pressure, a very large number of different changes may be caused to take place. Few of these lead to the production of single compounds, since change involves two or more stages and the conditions of the experiment, though at an optimum perhaps for one of these, may be far less favourable for the other. It is worth while summarizing the reactions very briefly, if only as an indication that nothing appears to be impossible with the aid of an appropriate catalyst. The standard reactions of alcohol are partial dehydration to ether and complete dehydration to ethylene:

$$2C_2H_5OH = (C_2H_5)_2O + H_2O$$
$$C_2H_5OH = C_2H_4 + H_2O$$

Alcohol is dehydrogenated to acetaldehyde and under some conditions to ketene:

$$C_2H_5OH = CH_3CHO + H_2$$
$$C_2H_5OH = CH_2CO + 2H_2$$

Decomposition.—When the vapour of alcohol is passed through heated tubes it undergoes decomposition, the nature of which depends on the temperature and the material of the tube. With glass at a temperature about 500° the products are ethylene by dehydration and acetaldehyde by dehydrogenation. At higher temperatures a secondary decomposition of the aldehyde to carbon monoxide and methane takes place.

In a glass tube at 800—830°, according to Ipatiev only 20% of the alcohol forms ethylene, the remainder being dehydrogenated, one-third of the aldehyde produced being decomposed. In a platinum tube at a lower temperature even more alcohol was dehydrogenated, but all the acetaldehyde was further decomposed. The same reaction in presence of catalysts has engaged the attention of a number of workers: it must suffice to summarize their results in the form of a table given by Morris.*

Action of metallic catalysts

Catalyst	Ethylene formed %	
ThO_2	100	
Al_2O_3	98·5	Dehydration catalysts
W_2O_3	98·5	
Cr_2O_3	91	
SiO_2	84	
TiO_2	63	
BeO	45	
ZrO_2	45	Mixed dehydration and dehydrogenation catalysts
U_2O_8	24	
Mo_2O_5	23	
Fe_2O_3	14	
V_2O_3	9	
ZnO	5	
MnO_2	0	
SnO	0	
CdO	0	
Mn_3O_4	0	Dehydrogenation catalysts
MgO	0	
Cu	0	
Ni	0	

Catalysts are of two types, the elementary, represented by the metals, and lattice catalysts, composed of compound materials, such as oxides etc., of which the surfaces contain an additional factor of variability. A definite and specific activity can be ascribed to each type of ion; thus, on the metal ion there will be hydrogenation and dehydrogenation, whereas on the oxide ion the processes are essentially hydration and dehydration.

The importance of the anion in determining the relative extents of dehydrogenation and dehydration is illustrated by data accumulated by H. S. Taylor at Princeton, showing the effect of salts of zinc and manganese on ethylalcohol. With an increase in the valency of the anion there is progressive change from dehydrogenation activity to dehydration activity:

Catalyst	C_2H_4	H_2	Catalyst	C_2H_4	H_2
ZnF_2	12	88	MnO	5	95
ZnO	9	91	$MnSO_4$	5	95
$ZnSO_4$	22	78	$Mn_3(PO_4)_2$	25	75
$Zn_3(PO_4)_2$	43	57	$Mn_2P_2O_7$	88	12
$Zn_2P_2O_7$	99	1			

The reaction products become very complex when alcohol is dehydrogenated to aldehyde when passed over zinc oxide or zinc chromite at 300° to 400°. Practically no aldehyde is produced, however, if the reaction takes place under a sufficiently high hydrogen pressure; instead of aldehyde various substances of higher molecular weight are formed. This subject has been particularly studied by Adkins and his students, and a summary of some of their results has been given by J. N. Pearce (J. Phys. Chem., 1932, 36, 2006).

* At the time of writing this section my work has been much facilitated by a paper by H. E. Morris in *Chemical Reviews*, 1932, 10, 465, in which copious references to the original literature will be found.

FINALE

I have traced my subject along a course which has been at least varied, trying to throw into relief the contacts between alcohol, the substance, and the progress of humanity, the growth of knowledge, and the application of chemistry to industry. It has been inspiriting to escape from the here and now before returning to the realities of the day. Scientists, alas, have to write of the realities rather than the poetry of life. There has always been progress, and so long as our foundations are sure we shall continue to advance. Through the ages the virtue of the moment has been the courage to experiment. To possess the courage to obtain the new through the knowledge of the old is undoubtedly the ideal in life.

PROF. P. DEBYE

Prof. P. Debye, the Faraday Lecturer of the Chemical Society for 1933, was born at Maastricht, Holland, in 1884, and received his education in that country. Subsequently he became assistant to Sommerfeld in Munich, where he took his doctorate. Since 1911 he has held chairs of physics at Zürich (1911—1912 and 1920—1927), Utrecht (1912—1914), Göttingen (1914—1920), and Leipzig, where he has been since 1927.

Few physicists during this century have made a larger contribution to chemical science than Debye. In 1912 he published his work on the atomic heats of solids, which was one of the early applications of quantum theory to chemistry. During 1916—1917, in conjunction with Scherrer, he developed the powder method of X-ray spectrum photography. The earlier methods of Laue and of Bragg required a well-formed crystal, the symmetry of which had to be known. In the Debye-Scherrer method microscopic or submicroscopic crystals were compressed into a small cylinder, and gave an X-ray spectrum, which they were able to interpret to give the crystal lattice. They applied their method to graphite and amorphous carbon, which

were shown to have the same structure, and then to tungsten powder. It has since been extended, and has become one of the most frequently used procedures.

In 1923 Debye and Huckel published their theory of electrolytes, which was a development of the inter-ionic attraction theory of Milner. *An entirely new outlook was introduced: ionization in solution was assumed to be complete at all dilutions: and deviations from the ideal behaviour were attributed to inter-ionic attractions.* The last ten years have witnessed numerous tests of this theory, and it has undergone considerable modification and amplification, but in essence it has come to replace almost completely the older conceptions of ionization in solution. Debye's work has been characterized throughout by a great interest in inter-ionic and intermolecular forces. The advances which have been made in recent years in the conception of polar molecules have been due in no small measure to theoretical and practical contributions by Debye and his pupils. In 1929 yet another development of great significance took place, when the method of studying the scattering of *X* rays by gaseous molecules was published. The distribution of the scattered radiation was shown to give rise to definite maxima, which were interpreted to give interatomic distances in the molecules of the scattering substance.

In view of Prof. Debye's lecture on "The Relations between Stereochemistry and Physics" at the Royal Institution on March 29, the foregoing will be of interest.

EXHIBITION OF PLASTICS

In connexion with the forthcoming Exhibition of Plastics at the Science Museum, South Kensington, the Plastics Group has arranged a series of 12 weekly lectures each dealing with some division of the industry or with some special application of plastics.

The list is set out below, and further details will appear at appropriate dates in the Calendar of Forthcoming Events.

Date	Author	Subject
April 12	Mr. H. V. Potter, B.Sc., F.I.C.	"Plastics and What they Are."
.. 19	Mr. A. J. Gibson	"Plastics: Shellac and Natural Resin Types and Their Uses."
.. 26	Mr. Foster Sproxton, B.Sc., F.I.C.	"Plastics: Celluloid and Casein Types and their Uses."
May 3	Mr. Kenneth M. Chance, A.M.I.E.E.	"Plastics: Urea-formaldehyde Types and Their Uses."
.. 10	Major H. C. Parker, M.B.E., A.M.I.E.E.	"Plastics and the Fabricator."
.. 17	Dr. L. A. Jordan, D.Sc., M.I.Chem.E.	"Plastics: Their Use in the Paint Industry."
.. 26	Prof. C. S. Gibson, O.B.E., M.Sc., F.R.S.	"Plastics: Their Use in Dentistry."
.. 31	Prof. G. T. Morgan, O.B.E., D.Sc., F.R.S.	To be arranged.
June 7	Mr. George Dring, B.Sc., F.I.C.	"Plastics: The Phenolic Types and their Uses."
.. 14	Dr. W. J. Jenkins, B.Sc., Ph.D.	"Plastics: Cellulose Esters and Ethers and their Uses."
.. 21	Mr. Raymond McGrath, A.R.I.B.A.	"Plastics and the Architect."
.. 28	Mr. K. G. Maxwell . . .	"Plastics: Their Use in the Electrical Industry."

SOCIETY OF CHEMICAL INDUSTRY

OFFICIAL NOTICES

ANNUAL MEETING, NEWCASTLE, JULY, 1933

We are able to publish much earlier than usual a forecast of the programme of the annual meeting which is being held by the invitation of the local section in Newcastle from Monday, July 10, to Friday, July 14. Arrangements are well forward. The details which are not actually fixed mainly concern visits to works and other excursions, and these will be announced in due course. Members should reserve the dates now and where possible should advise the local hon. secretary, Mr. J. W. Craggs, Green Lane Works, Pelaw-on-Tyne, as soon as possible of their intention to take part. This early notification is of great assistance to the local officials and is not taken as binding.

PROGRAMME

Monday, July 10.—Registration at Armstrong College. 7.30 p.m.—Informal gathering in King's Hall—Music, Dancing, and Light Refreshments.

Tuesday, July 11, 10 a.m.—Council Meeting in Council Room, Armstrong College. 11 a.m.—Annual General Meeting in Chemical Lecture Theatre. Civic Welcome by Lord Mayor. Welcome by the Principal Sir William Marris. PRESIDENTIAL ADDRESS. 1 p.m.—Lunch by invitation of the Newcastle Section either in Barras Bridge Assembly Rooms or in King's Hall, Armstrong College. 2.30 p.m.—Chemical Engineering Group Meeting. Papers by Messrs. King and Pearce. Simultaneously, Ladies' Excursions to places of interest in City. Arrangements made in conjunction with Society of Antiquaries. 8 p.m.—Civic Reception in Laing Art Gallery, New Bridge Street.

Wednesday, July 12, 9.30 a.m. to 11.—At Armstrong College, Plastics Group Meeting. Open to all. Addresses by Dr. B. Rassow, Leipzig, and other speakers. 11.15 a.m.—Presentation of Society's Medal and Address by Medallist. 12.15 p.m.—Visit to Roman Wall via Hexham or Chollerford. Take coaches at College Road. Lunch either at "The George," Chollerford, by invitation of Newcastle Corporation, or at Hexham. Return, arriving Newcastle 5.30 p.m. 7.30 p.m.—ANNUAL DINNER at Barras Bridge Assembly Rooms or at the Royal Station Hotel.

Thursday, July 13, 10 a.m. to 12.—Open Meeting of Food Group. Opening Address by Sir John Russell: "How Science can help the Nation to produce more of its own Food." 1 p.m.—Unofficial Lunch. 2 p.m.—Works Visits and Excursions. 8 p.m.—Reception by Sir William Marris, Sir Cecil Cockrayne, M.P., and College Council: King's Hall, Armstrong College. Music, Dancing, Buffet.

Friday, July 14, 10 a.m.—Start for visit to Imperial Chemical Industries at Billingham. Lunch and Tea provided at Billingham by the Company. Party limited to 100. Other works visits and excursions, probably including visit to Farne Islands.

"**History of the British Chemical Industry,**" by Stephen Miall. The Society still holds a small stock of Dr. Miall's "History" published in 1931. It is not likely that a second edition will be printed in the near future. These conditions make it undesirable to include the book on the permanent list of the Society's publications. The remaining copies will, therefore, be offered to members for purchase at 7s. 6d. per volume, post free. All orders should be accompanied by a remittance, and will be executed in rotation.

FOOD GROUP

A meeting of the Food Group of the Society was held at Burlington House on March 22, with Mr. B. G. McLellan presiding, when a number of short papers were read by members of the Group. Mr. E. Hinks opened the meeting with a paper on "Fifty Years of Retrogression in the Food Industry," and Dr. Julius Grant dealt with "Ultra-violet Light and Food Testing." Mr. G. F. Caley then gave a paper entitled "A Brief Outline and Explanation of the Pure Food Regulations of New South Wales." In his paper "On the Dating of Packages," Mr. A. L. Bacharach, of the Glaxo Laboratories, considered a suggestion which had been made by Dr. T. W. Naylor-Barlow at a previous meeting of the Group (cf. CHEM. & IND., Feb. 3, p. 102). Dr. J. W. Corran, of Messrs. J. & J. Colman Ltd.'s research department, then read a paper on "The Relative Effect of Spices and Related Substances on Yeast Fermentation," and Mr. J. W. Black dealt with "A Special Aspect of Factory Cleanliness" arising also out of a previous Food Group discussion. Dr. C. H. Lea then read a paper on "The Action of Light on Fats" and the meeting concluded with a paper by Dr. R. H. Callow, of the British Arkady Co., Ltd., on "The Application of the Combustion Method to the Study of Flour Conservation in Bread-making."

The time allowed for discussion was necessarily very short, but from the contributions made by members it was obvious that several of the papers, notably those of Dr. Grant, Mr. Bacharach and Dr. Corran, had aroused considerable interest. It is hoped to publish certain of the papers in subsequent issues of the JOURNAL.

NEWCASTLE SECTION

At a meeting of the Newcastle Section on March 9 the following officials and members of committee were elected: *Chairman:* Prof. G. R. Clemo; *Vice-Chairman:* Dr. J. T. Dunn; *Hon. Treasurer:* Mr. B. P. Hill; *Hon. Secretary:* Mr. J. W. Craggs; *Committee:* Dr. W. T. K. Braunholtz, Prof. H. L. Riley, Dr. A. A. Hall, Messrs. C. J. Ivison, D. W. Jones, E. M. Myers, P. D. Scott, H. Dunford Smith, F. H. Walker, W. A. Walmsley, and S. A. Wikner.

SOUTH WALES SECTION

The annual meeting of the South Wales Section was held at the Technical College, Cardiff, on Friday, March 17. The chair was taken by Dr. H. B. Watson, chairman of the Section.

The chairman referred to the loss the Section had sustained by the death of Prof. C. M. Thompson who was one of the founders of the Section.

The following officers were appointed for the ensuing year. *Chairman:* Mr. C. M. W. Grieb; *Vice-Chairman* Mr. W. Grey-Davies; *Hon. Secretaries:* Messrs. George Madel and Ernest A. Rudge; *Hon. Treasurer:* Mr. J. H. Wells; *Committee:* Prof. J. E. Coats, Messrs. W. H. Crighton, T. G. Watts, P. V. Lloyd, and Dr. H. B. Watson: *Representative on the Chemical Engineering Group:* Mr. J. H. Wells.

After the business of the meeting had been transacted the retiring chairman, Dr. H. B. Watson, addressed the members on the activities of the year.

CHEMICAL SOCIETY

The following is a summary of the continuation of the discussion on "The chemical constitution of œstrin" held on March 16. Following Dr. G. F. Marrian's opening contribution (see p. 268).

Mr. J. F. Danielli and Dr. N. K. Adam said: Surface pressure and surface potential measurements on derivatives of œstrin have shown that these substances spread on water to form very interesting types of unimolecular films, from which a good deal of information can be obtained as to the constitution of the molecules. The triacetyl derivatives of trihydroxyœstrin, and the diacetyl methyl ether, in which the phenolic hydroxyl group is methylated, form both gaseous and condensed films. In the gaseous films the molecules are lying flat in the surface; this shows that the phenolic group is in a part of the molecule remote from the two alcoholic hydroxyls. As these films are compressed the molecules stand on end, forming condensed films of area about 33 sq. Å.; since a larger pressure is required to cause the molecules of triacetylœstrin to stand on end than those of diacetylœstrin methyl ether, it is clear that the molecules are standing with the two adjacent *alcoholic* hydroxyls to the water. The area of 33 sq. Å. is so small that it is certain that the anchorage is by the end ring if the ring system, as appears probable, is of either the chrysene or the naphthacene type. Marrian's oxidative reactions show that the two alcoholic groups are either on a five carbon ring at the end of the skeleton, or on a six carbon ring in the middle; combining this with the above evidence from the films, it appears that the end ring carrying the hydroxyls is a *five carbon* ring.

The reduction product of ketohydroxyœstrin, in which only the phenolic hydroxyl group remains, forms a condensed film only, very similar to that formed by calciferol, of area about 47 sq. Å. at no compression, and somewhat compressible. It is practically certain that the hydroxyl group must here be in an end ring—those sterols (*e.g.*, pseudocholesterol) in which the hydroxyl is in the second ring give areas considerably larger than this. Hence the second end ring *must be benzenoid.*

These various derivatives provide a unique case, in which the same molecular structure can stand on either end, or lie flat, according to the distribution of polar groups.

Surface potential measurements show that the vertical component of the dipole moment of the molecules is much larger when the molecules are lying flat than when they are upright. The axis of the resultant dipole of the molecules is therefore much inclined to the plane of the

ring structure: probably also the two alcoholic groups are cis, not trans, thus reinforcing each other's dipoles.

Dr. J. D. Bernal: A year ago it was concluded from X-ray measurements and optical examination of crystals of trihydroxy- and ketohydroxy-œstrin that the œstrin molecule was flat and of dimensions approximately 4·5 × 7·5 × 11 Å. This would correspond to a structure of condensed ring type most probably chrysenoid. At that time a four ring system was considered impossible on chemical grounds, and only a phenanthrene skeleton was postulated. Since then further crystallographic work on sterols, bile acid and their derivatives, as well as on synthetic hydrocarbons, has shown that œstrin falls into place with all these compounds in regard to (140°) has a simple structure with two molecules per cell and a centre of symmetry in the molecule, and is therefore presumably the *trans* compound. The other, of m.p. 75°, has an altogether extraordinary structure with a real cell 7 times that of its apparent cell, and containing 64 molecules. This indicates extreme difficulties of regular packing for structures with *cis* arrangements and as no natural product so far examined shows such complexity, it is fair to suggest that all have a *trans* configuration with respect to the two central atoms of the ring system.

The following table summarises the results of *X*-ray and optical measurements on œstrin and allied substances.

Substance	Cell dimensions in A			β	Molecules per cell	Space group	Optical properties α	β	γ	Sign	Remarks
Trihydroxyœstrin	9·06*c*	7·50*a*	2 × 11·4*b*	112°	4	$P2_1$	⊥*a*	*a*	*b*	—	Molecules ‖ to symmetry axis *b*
Ketohydroxyœstrin α	9·06*c*	7·50*a*	2 × 11·0*b*	112°	4	$P2_1$	⊥*a*	*a*	*b*	—	Ditto
„ β	9·9*a*	7·7*b*	2 × 8·95*c*	90°	4	$P2_12_12_1$	*a*	*c*	*b*	+	Molecules are inclined to *c*∴*b* in direction of γ
Bromoketo-œstrin	9·0*a*	2 × 6·9*b*	12·8*c*	90	4	$P2_1a$	*a*	*b*		?	Bromine atom affects cell length.
Phenanthrene	8·60*a*	6·11*b*	2 × 9·62*c*	98°	4	$P2_1a$	⊥*c*	*b*	‖*c*	—	Molecules nearly ‖*c*
Chrysene	8·4*a*	6·2*b*	2 × 12·2*c*	106°	4	$P2_1a$	⊥*c*	*b*	*c*	—	Ditto
Octahydrochrysene	10·3*a*	7·15*b*	11·5*c*	127°	2	$P2_1a$	⊥*c*	*b*	‖*c*	—	Ditto
Hexahydrochrysene "*trans*"	11·0*a*	7·15*b*	8·05*c*	106°	2	$P2_1a$	Between *a* and *c*	*b*	Between *a* and *c*	?	Molecule inclined to *c*, hence low value.
Hexahydrochrysene "*cis*"	12·7*a*	14 6·6*b*	15·4*c*	90°	64	?	*a*	*b*	*c*	?	—

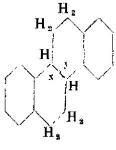
The axial lengths have been arranged so that they represent, in order, twice the thickness, the width, and the length of the individual molecules.

molecular width and thickness and optical properties, while differing somewhat in mutual arrangements of the molecules due to the presence of active hydroxy- or keto-groups at opposite ends of a four-ring structure.

Unfortunately it has been impossible to give more precise information as to the nature of the ring system in detail, particularly in relation to the 5 or 6 carbon character of ring IV. This would require a detailed intensity analysis of well-formed crystals, which were not available except for the orthorhombic variety of ketohydroxyœstrin, the symmetry of which is too high for unequivocal determination of the molecular shape. A similar difficulty prevented the data obtained from the study of bromoketo-œstrin from giving useful information. If it were possible to obtain crystalline hydrocarbons derived from œstrin, the problem could be tackled with very much more hope of success.

Meanwhile the study of the artificial hexahydrochrysenes prepared by Prof. Robinson has yielded some interesting indications on the steric nature of the central rings in the sterols and œstrin.

These compounds of formula



differ in the *cis* or *trans* configuration of the carbon atoms *x* and *y*. Of these the compound of higher m.p.

Prof. E. C. Dodds and Dr. J. W. Cook: Developments in the chemistry of œstrin suggested to us the desirability of testing for œstrogenic action synthetic compounds of somewhat allied structure. The activity of a number of compounds has now been established. The first of these, 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene, contains its keto-group in relatively the same position as the keto-group in œstrin, whereas phenanthrene derivatives with polar groups in positions 2, 3, and 4 proved inactive, as was also the case with a number of bile acid degradation products; among them was pyrodeoxybilianic acid. Correlation of œstrogenic activity with cancer-producing activity was achieved in the case of 9 : 10-dihydroxy-9 : 10-di-*n*-butyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene, which is derived from the carcinogenic but non-œstrogenic hydrocarbon, 1 : 2 : 5 : 6-dibenzanthracene. The activity of this di-*n*-butyl compound is of a very high order, but curiously enough the corresponding dimethyl compound is inactive. Moreover, two very potent carcinogenic hydrocarbons, 1 : 2-benzpyrene and 5 : 6-*cyclo*penteno-1 : 2-benzanthracene, have weak œstrogenic activity. Among the sterols and their derivatives, positive results were obtained with ergosterol, and more definitely neo-ergosterol and calciferol.

In testing these compounds the greatest care was taken to ensure that they really did reproduce the natural phenomena of the œstrus cycle. Using castrated rats, the technique followed was essentially that of Allen and Doisy, the modification employed being that of Allan, Dickens and Dodds. The substances (100 mg.) were administered in sesame oil (6 c.c.). This was administered either by the divided dose technique already

described or as three injections of 2 c.c. each on consecutive days. Examination of the vaginal smears began on the fourth day after the start of the injections and was continued twice a day. By this means a full œstrus is produced in the rat with the two compounds, 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene and the 9 : 10-dihydroxy-9 : 10-di-*n*-butyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene. Killing of the animals at the height of œstrus showed that the uterine changes are present in addition, so that the œstrus is indeed a full one. Quite independent confirmation has been obtained by the injection of the ketotetrahydrophenanthrene into capons. This work was done in conjunction with A. W. Greenwood of the Institute of Animal Genetics, University of Edinburgh, and it was shown that daily injection of the compound into capons produced conversion of the male plumage into female plumage, thus giving striking confirmation that this compound really did reproduce all the phenomena of the natural hormone.

These tests must at present be regarded merely as qualitative examinations. Attempts to convert them into quantitative ones are in progress, but great difficulty is experienced owing to the very grave obstacles encountered with regard to solubility etc. These substances are only soluble in oil, and the difficulties of oil absorption are well known to those experienced in this work. It is possible, however, to assign the following order of potency and to note that the first compound is very much more potent than any of the others. That is to say, there is a very great gap between the first and second, and also a gap between the second and the others. The activity of calciferol is roughly the same as that of the carcinogenic hydrocarbons.

Order of activity

(1) 9 : 10-dihydroxy-9 : 10-di-*n*-butyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene. (2) 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene. (3) neo-ergosterol. (4) 5 : 6-*cyclo*penteno-1 : 2-benzanthracene. (5) 1 : 2-benzpyrene. (6) calciferol. (7) ergosterol.

Dr. A. Butenandt communicated the following:

Contribution to the Constitution of the Follicular Hormone (*Œstrin*).* [By A. Butenandt, H. A. Weidlich, and H. Thompson.]

On the basis of the experimental evidence hitherto available, formula (I) has been assigned to ketohydroxyœstrin, $C_{18}H_{22}O_2$, and formula (II) to trihydroxyœstrin, $C_{18}H_{24}O_3$ (Butenandt, Die Naturwissenschaften, 1933, **21**, 49). Some features of these structural formulæ depended upon the assumption, as a working hypothesis, of a close biological relationship between œstrin, the sterols and bile acids, and pregnandiol (Butenandt, Ber., 1930, **63**, 659; 1931, **64**, 2529) and still lacked experimental verification. In particular, proof was required of (1) the condensation of rings A, B and C as in the phenanthrene ring-system; (2) that ring A, and not ring B, is the aromatic ring to which is attached the phenolic hydroxyl group; (3) the position of the methyl group; and (4) the positions of attachment of the 5-membered ring and the relative positions within this ring of the carbonyl group (formula I) or of the two hydroxyl groups (formula II).

We have now carried out a series of degradation experiments which give considerable support to formulæ I and II.

As shown by Marrian and Haslewood (Chemistry and Industry, 1932, **51**, 277 T) and by Doisy (J. Biol. Chem., 1933, **99**, 327), trihydroxyœstrin (II) is converted by alkaline fusion into a phenolic dicarboxylic acid $C_{18}H_{22}O_5$ (III). The two carboxyl groups can arise only by fission of the 5-membered ring between two *secondary* carbinol groups, and they probably occupy the 1 : 5-positions with respect to one another. Ketohydroxyœstrin (I) is not an intermediate product, for under the same conditions it yields other products which will be described later. We have found that this acid (III), on dehydrogenation with selenium, eliminated carbon dioxide and passed smoothly into a *dimethylphenanthrol*, m.p. 190—191° (Found: C, 86·32; H, 6·47. $C_{16}H_{13}OH$ requires C, 86·48; H, 6·30%). This dimethylphenanthrol, to which we assign formula IV, was purified through its *benzoyl derivative*, m.p. 210° (Found: C, 84·70, 84·40; H, 5·71, 5·66. Calc., C, 84·66; H, 5·52%), and was further characterised by the preparation of its *methyl ether*, m.p. 153° (Found: C, 86·39; H, 6·77. Calc., C, 86·44; H, 6·79%). Attempts to obtain derivatives of the *ortho*-quinone (V) from the benzoate or methyl ether by oxidation with chromic acid, in order to exclude the possibility that the hydroxyl group is attached to ring B, were unsuccessful with the amount of material which was available.

By distillation with zinc dust, the dimethylphenanthrol (IV) was smoothly converted into a dimethylphenanthrene, m.p. 140° (Found: C, 93·13; H, 7·09. $C_{16}H_{14}$ requires C, 93·20; H, 6·80%), which yielded an orange-red *picrate*, m.p. 148° (Found: N, 9·71. Calc., N, 9·71%). This same 1 : 2-*dimethylphenanthrene* (VI), hitherto unknown, was prepared synthetically by the method developed by Haworth (J. Chem. Soc., 1932, 1126) for the synthesis of homologues of phenanthrene (formulæ VII—IX); the synthetic hydrocarbon corresponded in all its properties with the substance obtained from the hormone.

In order to obtain evidence of the relationship assumed to exist between the hormone and the sterols and bile acids, we attempted also to obtain 1 : 2-dimethylphenanthrene (VI) from ætiobilianic acid (X); 80 mg. of this bile acid derivative, rendered available by the elegant degradation of cholanic acid described by Wieland, Schlichting and Jacobi (Z. physiol. Chem., 1926, **161**, 80), was dehydrogenated with selenium in a closed vessel. From the reaction mixture was isolated 3 mg. of 1 : 2-dimethylphenanthrene picrate, m.p. 148°, alone or mixed with the product prepared from trihydroxyœstrin. The hydrocarbon yielding this picrate did not depress the m.p. of 1 : 2-dimethylphenanthrene; crystallographic examination of these substances is being undertaken.

In our opinion, the results so far obtained justify the following conclusions:

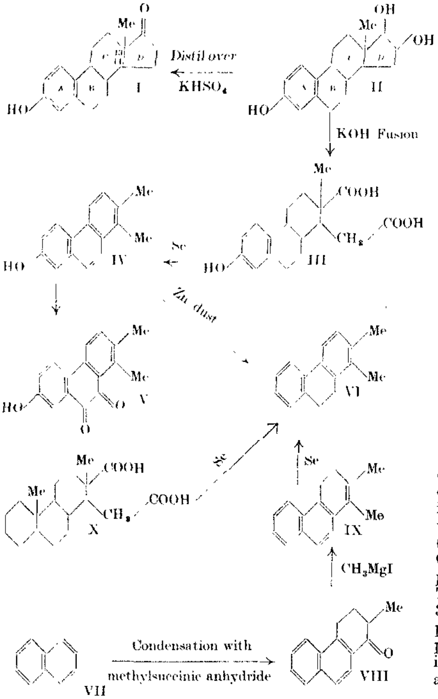
(1) Rings A, B, and C of the œstrin molecule are condensed in the form of a *partially hydrogenated*

* Chemisches Universitätslaboratorium, Göttingen.

phenanthrene ring-system, and a *5-membered* ring is fused on to this.

(2) The methyl group is attached to carbon atoms 13 or 14 of the reduced phenanthrene ring-system.*

(3) As one of the two methyl groups of the phenanthrene (VI) originates in the acetic acid residue of the dicarboxylic acid (III), it follows that at least one of the two carbon atoms which bear the methyl groups of the dimethylphenanthrene must be a point of attachment of the 5-membered ring D.



(4) The carbonyl group of ketohydroxyœstrin is situated in the *terminal* 5-membered ring D.† In trihydroxyœstrin two *adjacent secondary* alcoholic groups occupy a corresponding position.‡

(5) The close relationship between the œstrins and the sterols and bile acids receives support from the isolation of the same dimethylphenanthrene from both trihydroxyœstrin and ætiobilianic acid.

* Using the system of numbering usually adopted for the sterols (see formula I).

† Adam and Danielli (Biochem. J., 1932, **26**, 1233) arrived at the same conclusion from their surface film experiments.

‡ This inference has already been regarded as extremely probable by Marrian and by Doisy (*loc. cit.*).

We are seeking confirmation, by synthesis, of the position of the hydroxyl group in the dimethylphenanthrol (IV), and therefore of the aromatic ring in œstrin. We are also engaged in experiments designed to establish the second point of attachment of ring D, and of the relative position of the carbonyl group within this ring.

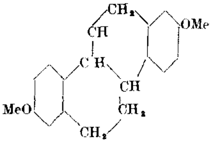
Dr. H. King, speaking on behalf of Dr. Rosenheim and himself, drew attention to the group of C_{18} hydrocarbons which have been obtained from œstrin, sterols and bile acids by various methods of dehydrogenation as shown in the table on p. 291.

It seems that drastic methods of dehydrogenation such as with palladium–charcoal or zinc, tend to produce chrysene, $C_{18}H_{12}$, whereas the less drastic selenium method regularly yields $C_{18}H_{16}$ (m.p. 125°), which must therefore represent some definite chemical entity. Through the kindness of Dr. Cook we have been able to examine a specimen of this hydrocarbon (from cholesterol) and to confirm its composition. It cannot be dehydrogenated to chrysene (Ruzicka and Thomann) and we find that it is reasonably stable to permanganate in boiling acetone. We have previously reported that its ultra-violet absorption spectrum is strikingly similar to that of retene (*1-methyl-7-isopropylphenanthrene*) and have drawn the conclusion that it contains a phenanthrene nucleus. We now consider that its constitution may be represented as that of a methyl-1 : 2-*cyclo*pentenophenanthrene. Its low melting point and stability towards permanganate are significant and are in accord with its formulation as a substituted hydrindene. The positions 10 : 13 for the methyl *groups attached to quaternary carbon atoms in ergosterol* is the simplest arrangement which explains the formation of toluenetetracarboxylic acid on oxidation with nitric acid, so that the formation of a methyl-1 : 2-*cyclo*pentenophenanthrene from such an allocation of methyl groups by selenium dehydrogenation must involve some special mechanism. We suggest that when the side-chain at C_{17} is removed from ergosterol (cholesterol or cholic acid) by selenium the methyl group C_{13} takes up the adjacent vacant position on C_{17}, thus preserving the saturation of the 5-membered ring IV. The hydrocarbon $C_{18}H_{16}$ (m.p. 125°) on this view is 3-methyl-6 : 7 : α : β : -naphthohydrindene. The same position of the methyl group is pictured in a forthcoming publication by Prof. Windaus (private communication), in preference to the improbable position on C_{13} previously assumed by him.

The hydrocarbon $C_{18}H_{14}$? (*m.p.* 243°), *obtained in* small amount by Butenandt from œstrin with zinc dust, and by Ruzicka and Thomann from cholic acid with selenium, may be impure chrysene. Ruzicka and Thomann's compound is admittedly impure and the high m.p. of both substances, coupled with Butenandt's statement that his hydrocarbon is stable to boiling permanganate, support such a view. The formation of chrysene from œstrin by zinc dust is analogous to the formation of chrysene from cholesterol by the same reagent and in both cases is clearly due to ring enlargement under the drastic conditions employed.

			$C_{18}H_{12}$	M.p.
Diels *et al.*	(1927)	Cholesterol and PdC	Chrysene	246—248°
Diels and Karstens	(1930)	Cholic acid ,, Se	Chrysene	250°
Raudnitz *et al.*	(1932)	Cholesterol ,, Zn	Chrysene	252°
Diels *et al.*	(1927)	Cholesterol and Se	$C_{18}H_{16}$	123—124°
Diels and Karstens	(1930)	Ergosterol ,, Se	$C_{18}H_{16}$	124—125°
Jacobs and Fleck	(1932)	Cholesterol ,, Se	$C_{18}H_{16}$	123—125°
Ruzicka and Thomann	(1933)	Cholic acid ,, Se	$C_{18}H_{16}$	124—125°
Ruzicka and Thomann	(1933)	Cholic acid and Se	$C_{18}H_{14}$	230—240°
Butenandt	(1932)	Œstrin ,, Zn	$C_{18}H_{14}$	234° / 243°

Prof. R. Robinson said that, in common with all other organic chemists, he had the greatest admiration of the work of Dr. Marrian in this field, and in view of the small quantities of the pure hormone which have been available it was remarkable how much had been achieved. In reply to Dr. Bernal, he said that it was true that the specimens of hexahydrochrysene had been wrongly labelled. The diphenyladipic acids were first prepared by Henle in 1906, but it was only recently that their configuration had been established by Vogel. The acid characterised by the latter as the *meso*-βγ-diphenyladipic acid yields ultimately the *trans*-hexahydrochrysene, whilst the *rac*-diphenyladipic acid furnishes *cis*-hexahydrochrysene. Thus Dr. Bernal's deductions from the physical properties were perfectly correct. Mr. Ramage has continued his work on the synthesis of hexahydrochrysenes and has now obtained a dimethoxyhexahydrochrysene of the annexed constitution:



It will be observed that this structure is quite closely related to the formula for the œstrins based on the presumed analogy to the sterols. Prof. Robinson further remarked that the very interesting work of Butenandt and his colleagues (among whom he was gratified to find the name of H. W. Thompson) does not determine the position of the angle-methyl group since the *o*-dimethylphenanthrene may result from the transformation of a *gem*-dimethyl compound by a process analogous to many observed by Bamberger, by Crossley, and by others.

Mr. E. M. Meade said: One point of rather fundamental structural significance which arises out of the *X*-ray data is that since the "molecular thicknesses" of these compounds are so similar, the œstrins and sterols must, like chrysene, be almost uniplanar. Considering *cis* 1 : 2 fused rings, a fully hydrogenated naphthacene can have the structures

(I) (II) or (III)

all angles being 120°. Even (III) shows too great a thickness to accord with the data given. The only way in which to explain the results is that the sterols, œstrins, and hydrogenated naphthacene used for purposes of illustration must consist of all four rings linked in the *trans*-positions as in *trans*-decalin, represented thus: in "transverse section" as in the above formulæ.

Dr. G. F. Marrian, in summing up the discussion, first offered his very sincere congratulations to Dr. Butenandt on a magnificent piece of work. Clear proof of the relationship of the œstrous to the sterol group was now available and the structure of the œstrous could now be regarded as very nearly settled. Even if knowledge of this work of Dr. Butenandt had been in his possession before the discussion, he would still have made the same comments about the speculative formulæ which have previously been published. He had no objections to the adoption of speculative formulæ as the basis for a working hypotheses; he had already done this himself. He did, however, wish to point out that there was previously no justification for the publication of such formulæ as if they were well established, without any mention being made of the fact that they were based on speculation. Whether or not the speculation was intelligent was entirely beside the point.

Finally, Dr. Marrian drew attention to the great importance of the work of Dr. Cook and Prof. Dodds and pointed out that a wide field of research was now opened up in investigating more fully the physiological action of these synthetic œstrogenic substances.

OBITUARY

PROF. J. M. THOMSON

Chemists in this country and many other parts of the world will learn with deep regret of the death on March 22, at the age of 84, of Dr. John Millar Thomson. Not only was he a distinguished chemist, but he took also an active interest in the affairs of members of the profession, and his name will be honoured particularly by several generations of students at King's College, London, of which he was appointed Emeritus Professor of Chemistry in 1914, after an association going back to 1871.

Born in Glasgow in 1849, Thomson was educated at Glasgow High School and studied at Glasgow University, by whom he was later awarded the degree of LL.D. At the age of 22 he joined the Chemistry Department of King's College as an assistant demonstrator and became senior demonstrator eight years later. From 1880 to 1887 he served as professor of chemistry at Queen's College, London, but then returned to King's as Daniell Professor and head of the chemistry department. He remained with the College until his retirement in 1914, and during the last nine years of his office held also the position of vice-principal. In

recognition of his services a medal which bears his name is now awarded annually to a student in the final year of the special honours course in chemistry at King's College.

During the whole of his long career he took a leading part in the chemical associations in this country, the Chemical Society and the Institute of Chemistry being particularly indebted to him for many years of work. He was president of the Institute from 1900—1903, vice-president in 1894—97, 1903—6, and 1910, and honorary registrar for six years beginning in 1894. He became a member of the Council of the Chemical Society, in 1880, served as honorary secretary from 1883—97, was appointed vice-president in 1898—1901 and 1923—26, and was a member of the Council for many years. Between the years 1879 and 1913 he took a leading part in the activities of the Chemical Section of the Society of Arts. In 1897 he was elected a Fellow of the Royal Society, thereby following in the footsteps of his father and grandfather.

His contributions to the knowledge of chemistry are best illustrated by the many papers of which he was the author. These deal with the composition and optical properties of double nickel-cobalt salts, the action of nuclei on the crystallization of super-saturated solutions, the chemistry of pigments and of building materials, putrefaction and antisepsis, and the composition of ancient glasses, whilst he contributed articles to many scientific journals.

The funeral took place at Hampstead on March 27, those present including Dr. W. R. Halliday (principal, King's College, London), Prof. J. F. Thorpe (president, Institute of Chemistry), Prof. H. E. Armstrong (representing the Royal Society), Mr. Richard Pilcher (registrar of the Institute of Chemists), Prof. P. H. Kirkaldy and Dr. Bernard Dyer (representing the Society of Public Analysts), Mr. S. T. Shovelton (secretary of King's College), Dr. J. A. Voelcker (representing the Royal Agricultural Society of England), Mr. H. L. P. Myles (representing the University of Glasgow), Mr. S. E. Carr (assistant secretary, the Chemical Society), Mr. F. W. Clifford (representing the Chemical Society's Library), Sir Herbert and Lady Jackson, Dr. D. Somerville (late of King's College), Prof. D. M. Blair, Prof. S. A. F. White, Prof. A. J. Allmand, Prof. S. Smiles, Mr. R. L. Collett, Mr. Grant Hooper, Mr. W. Macnab, Dr. T. A. Henry, Prof. H. G. Atkins, and Mr. E. W. Timmis.

CORRESPONDENCE

ELECTRONIC STATES OF MOLECULES CONTAINING THE CO GROUP

SIR,—In the recent discussion of the Chemical Society upon the Raman effect, I put forward some tentative views upon the state of the electrons in the CO group of aldehydes and ketones. It is now possible to make a more definite hypothesis; since the problem is ultimately of importance for chemical ideas upon valency and reaction, I should like to give the bare outline of the theoretical and spectroscopic position.

Following Mulliken's general treatment of polyatomic molecules (Phys. Rev., Feb. 15, 1933) one can combine the wave functions of CH_2 in a ^3B state and of oxygen in its ground state and arrive at formaldehyde H_2CO in an ^1A state, which seems very probable as the normal state of the molecule. The binding between C and O will be $[x + x][z + z]$ very much the same as the binding between the C and C in C_2H_4. That is, one arrives at a reasonable description of the chemical double bond, which will be substantially the same *through the CO groups of all aldehydes and ketones* (from the spectroscopic evidence).

The first excited state of formaldehyde will be a ^3B state. Here instead of having two closed electron pairs, we have a single electron pair and two unpaired electrons. It is probable that the absorption bands in formaldehyde (and all aldehydes and ketones) found near 3000 Å.U. represent a transition from the ground state (^1A : with two electron pairs between C and O) to this first excited state (^3B : with one electron-pair). The low intensity of these bands, which are 10^{-3} to 10^{-4} times as strong as the short wavelength bands of aldehydes and ketones, is strong evidence in favour of their being an intercombination $^1A \rightarrow {^3B}$.

This theoretical picture of the effect of light in the CO groups seems to harmonize well with the chemical facts and ideas. The theory shows promise of giving an interpretation of the structure, photochemical reactions, and ordinary chemistry of CO compounds in general.

I am, Sir, etc.,
P. C. SNOW

Cambridge
Mar. 22, 1933

ALCOHOL THROUGH THE AGES

SIR,—In his interesting article on "Alcohol through the Ages," in the last number of CHEMISTRY AND INDUSTRY, Dr. E. F. Armstrong, referring to the use of the word "alcohol" to indicate an impalpable powder, implies that Sir H. Davy used the term "alcohol of sulphur" to indicate flower of brimstone (p. 251, col. 1). This however, is a mistake, although the statement is to be found in the Oxford Dictionary. In fact, the alcohol of sulphur to which Davy refers was carbon bisulphide. I have not the 1812 edition at hand, but in Davy's *Collected Works*, 1840, iv, p. 229, he says: "Carbon and sulphur combine with each other and form a very peculiar compound, which was called by its discoverer, Lampadius, alcohol of sulphur. . . . The alcohol of sulphur or sulphuret of carbon. . . ." There can be no doubt from this that Davy did not mean flowers of sulphur.

I am, Sir, etc.,
T. S. PATTERSON

Glasgow University
Mar. 24, 1933

PERSONAL AND OTHER ITEMS

The University of London has awarded the degrees of D.Sc. (biochemistry) to Mr. H. G. Norman, of the Rothamsted Experimental Station, and D.Sc. (chemistry) to Mr. E. L. Smith, student of Chelsea Polytechnic.

We deeply regret to announce the death on March 27 of Mr. Hugh C. Clanahan, a member of the Society since 1885. Mr. Clanahan, who was 76 years of age, was a partner and director of the firm of Bayley, Clanahan & Co.,

chemical manufacturers, of Manchester, until his retirement at the beginning of this year. He was chairman for many years of the Manchester Importers' and Exporters' Association, resigning from the position two years ago, was an old member of the Manchester Reform Club, and was a prominent churchman and public worker.

We regret to learn of the death on March 22 of Col. C.M. Abercrombie, C.M.G., C.B.E., advertising manager of David Moseley & Sons, Ltd., india rubber manufacturers, of Manchester.

Bristol Section and Food Group

The first joint meeting of the Bristol Section and the Food Group will be held on Thursday, April 6, at 7.30 p.m. in the Chemical Department, The University, Bristol. Two papers will be given by Messrs. P. T. H. Pickford and V. L. S. Charley on "The Problems of the Cider Maker." A visit has been arranged in the afternoon at 2.30 p.m. to the Agricultural Research Station (The National Fruit and Cider Institute) at Long Ashton, by courtesy of the director, Prof. B. T. P. Barker, M.A. Members wishing to take part in this visit should notify Mr. Arthur Marsden, "Carn Brea," Bishop Road, Bishopston, Bristol, not later than Wednesday, April 5.

Association of British Chemical Manufacturers

The A.B.C.M. has published a handy index to the Acts of Parliament and Statutory Rules and Orders affecting the Chemical Industry. It may be obtained from the Association at the cost of sixpence.

Newcastle Chemical Industry Club

Mr. B. P. Hill occupied the chair at the annual general meeting when Dr. J. T. Dunn was unanimously elected president of the club. Prof. G. R. Clemo, Mr. Clive Cookson, and Mr. Arthur Kelly were elected vice-presidents, Dr. G. P. Lishman was elected chairman of committee, and F. H. Walker hon. secretary. Mr. B. P. Hill, the retiring chairman, moved a vote of thanks to those who had contributed to the library during the past year, and emphasized the usefulness of the library to local industries.

Institution of Mining and Metallurgy

The Gold Medal of the Institution of Mining and Metallurgy, the highest distinction in its power to confer, has been awarded to Sir John Cadman in recognition of his work in the advancement of technical education and the development of the mineral industries, and of his distinguished public services. Sir John Cadman is well known as an authority on mining problems; he has served as consulting petroleum adviser to the Government, and as a member of the Council of the Department of Scientific and Industrial Research.

Royal Society of Arts Prizes

A prize of £100 is offered by the Royal Society of Arts for an essay on the subject of fire at sea, its possible causes, preventive measures, means of detection, and treatment when once started. A prize is also offered for a valuable improvement in the science or practice of navigation proposed or invented during the years 1932—33; this prize is offered following the founding of a memorial to Thomas Gray, C.B., for many years assistant secretary of the Board of Trade, under the will of his son, Mr. Thomas L. Gray. The essays must be sent before December 31 this year to the secretary of the Royal Society of Arts, John Street, London, W.C.2.

Aviation Petrol from Coal

The Air Ministry has placed a contract for twelve months' supplies of a petrol produced by Low Temperature Carbonisation, Ltd. as a by-product in the manufacture of smokeless fuel. The petrol, which is refined by Messrs. Carless, Capel, & Leonard, of London, is stated to have a very high anti-knock value, making it suitable for modern high-compression engines running under service conditions. An entire home squadron of high-performance fighting machines is now flying solely on this petrol.

A New Use for Rubber

A new rubber-base product, with the name "Plioform" has recently been announced by the Goodyear Tire & Rubber Co. of America. It is stated that this material is entirely suitable for table-ware, as it is tasteless and odourless, is resistant to scratches, and is unbreakable. It is manufactured from pale crêpe rubber, which is dissolved in a solvent and chemically treated to give a white resinous compound which can be moulded to give articles of a light amber colour, or mixed with a filler and pigment and milled. The material also possesses good non-conductive properties, which makes it suitable for moulded electrical parts.

South Suburban Gas Co. Bill

After consideration for several days of the Bill promoted by the South Suburban Gas Co., for empowering the company to charge differential prices for gas in certain parts of its limits of supply, the House of Lords Select Committee has announced that the preamble of the Bill was not proved as regards Clause 4, which set out the main object of the Bill, which is therefore to be dropped. The decision affects nine of the eleven claims of the Bill, and the company can, if it wishes, put the remaining two clauses in a new Bill.

COMPANY NEWS

JOHN KNIGHT, LTD.

The net profit of John Knight, soapmakers, controlled by Lever Bros., was £272,590 during 1932, comparing well with the previous year's profit of £258,522. A final dividend on the ordinary shares has been announced of 25%, bringing the total for the year to 45%, an increase of 15% on last year.

DORMAN LONG & CO., LTD.

It was officially announced on March 23 that a provisional agreement had been reached by the directors of Dorman Long & Co. and the South Durham Steel & Iron Co. for an amalgamation of their interests. The scheme, which is dependent upon the consent of debenture and shareholders of the companies, will bring together capital totalling more than £18,000,000.

CELANESE CORPORATION OF AMERICA

The earnings statement of the corporation for 1932 shows a net profit from operations of $1,596,162 as compared with $1,537,181 for 1931. It has been decided to place $100,000 to reserve for contingencies and, after provision for depreciation etc., a net income remains for distribution of $891,866. Special reserve arising from change in capital, amounting to $1,732,722 at December 31, 1931, has now been appropriated and utilized for the purposes for which it was created.

MARKET REPORT

This Market Report is compiled from special information received from the manufacturers concerned.

Unless otherwise stated, the prices quoted below cover fair quantities net and naked at sellers' works.

The following alterations in prices are reported since the publication of the last Market Report (cf. CHEM. & IND., Mar. 3, 1933, p. 189).

GENERAL HEAVY CHEMICALS

Sod. Phosphate. £12 10s. per ton, f.o.r. London, casks free. Sod. Silicate 140° Tw.—Spot, £8 5s. per ton d/d station, returnable drums. Sod. Sulphate (Glauber's Salt)—Spot, £4 2s. 6d. per ton d/d. Sod. Sulphide solid, 60/62%.—Spot, £10 15s. per ton, d/d in drums. Crystals, 30/32%.—Spot, £8 per ton, d/d in casks. Sod. Sulphite, Pea Cryst.—Spot, £13 10s. per ton, d/d station in kegs; Commercial.—Spot, £9 10s. per ton, d/d station in bags.

TAR PRODUCTS

Acid Cresylic, 99/100.—11d.—1s. 8d. per gal. according to specification. Refined, 1s. 7d.—1s. 8d. per gal. Pale, 98%. 1s. 2d.—1s. 3d. per gal. 95%. 11d.—11½d. per gal. Dark, 10d. per gal.

Creosote. B.S.I. specification, 2½d.—3d. per gal., d/d. Heavy—4d. per gal.

Pitch, medium, soft.—90s. per ton, in bulk at makers' works.

Toluole.—90%, 2s.—2s. 1d. per gal. Pure, 2s. 4d. per gal.

PHARMACEUTICAL AND PHOTOGRAPHIC MATERIALS

Menthol.—A.B.R., recryst., B.P., 15s. 6d. per lb. net. Synthetic, 8s. 6d.—12s. per lb. Synthetic detached crystals, 8s. 6d.—10s. per lb., according to quantity; Liquid (95%), 8s. 6d. per lb.

PERFUMERY CHEMICALS

Aubepine (*ex Anethole*).—8s. per lb.

Amyl Acetate.—2s. 3d. per lb. Amyl Butyrate.—4s. per lb. Amyl Cinnamic Aldehyde.—8s. 3d. per lb. Amyl Salicylate.—2s. 9d. per lb. Anethol. 21/22° C., 4s. 9d. per lb.

Benzaldehyde free from Chlorine.—2s. 9d. per lb.

Benzyl Acetate from Chlorine-free Benzyl Alcohol.—2s. per lb. Benzyl Alcohol free from Chlorine.—2s. per lb. Benzyl Benzoate, 2s. 3d. per lb.

Cinnamic Aldehyde.—Natural, 12s. 3d. per lb.

Coumarin.—15s. per lb.

Ethyl Cinnamate.—8s. 6d. per lb.

Eugenol.—7s. 6d. per lb. Geraniol (Palmarosa).—17s. per lb. Geraniol.—6s. 6d.—11s. per lb. Heliotropine.—6s. per lb. Iso Eugenol.—9s. per lb. Linalol.—(*ex Bois de Rose*) 6s. 9d. per lb.—(*ex Shui Oil*) 6s. per lb. Linalyl Acetate.—(*ex Bois de Rose*) 8s. 3d. per lb.—(*ex Shui Oil*) 7s. per lb.

Methyl Anthranilate.—9s. per lb.

Methyl Benzoate.—4s. 6d. per lb.

Musk Ketone.—33s. per lb.

Musk Xylol.—8s. per lb.

Nerolin.—5s. per lb.

Rhodinol.—60s. per lb. Safrol.—1s. 7d. per lb. Terpeneol.—2s. per lb. Vanillin (*ex Clove Oil*).—16s.—18s. per lb.—(*ex Guaiacol*)—14s. 3d.—16s. 3d. per lb.

ESSENTIAL OILS

Almond.—Foreign S.P.A., 9s. 6d. per lb. Anise.—2s. per lb. Araucaria, 9s. per lb. Bergamot.—6s. 9d. per lb. Bourbon Geranium, 26s. per lb.

Camphor.—Brown, 85s. per cwt. White, 90s. per cwt. Cananga, Java, 10s. 9d. per lb. Cinnamon Oil.—4s. per lb. Cassia, 80/85%, 4s. 9d. per lb.

Eucalyptus. Australian B.P., 70/75%.—1s. per lb. Lavender.—Mont Blanc, 38/40%.—10s. 6d. per lb. Lemon.—4s. 3d. per lb. Lemongrass.—2s. 10d. per lb. Orange, Sweet.—6s. per lb. Otto of Rose.—Anatolian, 37s. 6d. per oz.; Bulgarian, 55s. per oz. Palma Rosa, 9s. 6d. per lb.

Peppermint.—Japanese, 6s. 9d. per lb. Wayne County, 14s. per lb. Petitgrain.—6s. per lb.

Sandalwood, Mysore.—30s. per lb. 90/92%, 20s. per lb. Australian, B.P. and French Codex, 92/95%, 16s. per lb.

GENERAL NOTES

Official Trade Intelligence

The Department of Overseas Trade (Development and Intelligence), 35, Old Queen Street, London, S.W.1, has received the following inquiries for British goods. British firms may obtain further information by applying to the Department and stating the specific number. *British India:* Crude oil engines (5 h.p. and under) (424). *Latvia:* Bitumen and bitumen emulsion (B.X. 7528). *Sweden:* Industrial chemicals (441). *Syria:* Tinplate (445).

Key Industry Duty

The Treasury has made an Order, which will shortly be published by H.M. Stationery Office, under Section 10 (5) of the Finance Act, 1926, exempting carbolic acid (synthetic) from key industry duty. The order dates from March 15, 1933, to December 31, 1933.

Brotherton & Co., Ltd.

Brotherton & Co., Ltd., the chemical manufacturers of City Chambers, Leeds, have opened a branch office in London, the address of which is 68, Victoria Street, S.W.1. The office will be under the administration of Capt. B. L. Ratcliffe, M.C., who is a director of the firm.

Howards & Sons, Ltd.

The works, warehouses, and offices of Howards & Sons, Ltd., the chemical manufacturers of Ilford, will be closed for the Easter holiday from Thursday evening, to Tuesday morning, April 13 to 18.

The Chemical Catalog Co. Inc.

From now until May 1, 1933, the Chemical Catalog Co., Inc., of 330, West 42nd Street, New York, whose publications are well known to all scientists, is offering many useful books at 40% discount from the ordinary list prices. The books offered comprise a scientific and technological series, including several volumes of Colloid Symposium Monographs and the Annual Survey of American Chemistry as well as many publications on subjects connected with chemical engineering, and a series of monographs of the American Chemical Society. The company's offer provides an excellent opportunity to add to libraries at low cost, the accounts of much valuable works in America.

Tangyes, Ltd.

Mr. G. N. Guest, late managing director of Hollings & Guest, hydraulic engineers and John Hands & Sons, power press manufacturers, has, with other members of his staff, now joined the firm of Tangyes, Ltd., who state that they will be glad to quote for all types of hydraulic machinery and power presses.